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Some Halogen Substitution Products
of Benzoin Sulphide.

Dissertation
presented for the degree of Doctor of
Philosophy to the Board of University
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by
Rudolf de Roodt.

1890.

Note of Acknowledgement

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Rudolf de Roode.

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Introduction.

In a paper published in the American Chemical Journal No. 9. p. 229. Reusser and Bayley describe a method of preparation and the properties of para-brom-cetylbenzide. Its most characteristic property was that it possessed two separate and distinct tastes, a sweet and a bitter. The substance was made the subject of an investigation by Drs. Howell and Kastle of the Johns Hopkins University, and in a paper entitled "On the Nerve of Taste" it was shown by them that the nerves in the tip of the tongue are of a different character from those in the back part of the

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tongue, and that on the tip of the tongue the substance is only sweet while on the back part of the tongue it is only bitter.

The faculty of the Johns Hopkins University also prepared para-chlor-sulphuric acid, in order to ascertain if it had a similar effect upon the nerves of taste. It was found to possess both tastes in a more marked degree than did para-brom-sulphuric acid.

The object of this research was to investigate the other para-halogen-sulphuric acids, and the substances from which they were made and to observe their effect upon the nerves of taste. It was thought that some definite relation might be found to exist between the intensity of the taste and the chemical nature of the halogen contained in the sulph.

inide. Since para-brom-sulphamide was both sweet and bitter, and para-chlor-sulphamide was more sweet and more bitter it seemed probable that para-fluor-sulphamide would be still more sweet & still more bitter, while para-iodo-sulphamide would not be either as sweet or as bitter as the brom-sulphamide. We would thus have a series running thus.

Para-fluor-sulphamide	=	SWEET . BITTER
.. chlor ..		SWEET . BITTER
.. brom ..		SWEET . BITTER
.. iodo ..		SWEET . BITTER

As regards this point, however, it may be at once stated that no such definite relation was found to exist, for para-fluor-sulphamide was almost purely sweet, fully as sweet as benzene sulphamide, with only a very slight bitter after-taste; and para-iodo-sulph-

inside had very little taste at all and that was purely bitter; so that the series could run thus:

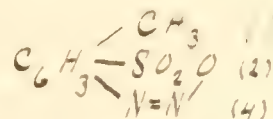
Para-fluor-sulphonide =	SWEET	Bitter
.. chlor ..	Sweet	Bitter
.. brom ..	Sweet	Bitter
.. iodo ..	—	Bitter

It therefore appears that no definite relation exists between the strength, or chemical activity, of the substituting halogen and the taste of the corresponding substance.

The diazo compound which formed the starting point in these investigations, was made by starting with para-nitro-toluene, converting this into the ortho-sulphonic acid, which by reduction with tin and hydrochloric acid, passes over into para-toluidine-sulphonic acid from which the diazo compound was made.

Para-di-azo-toluene-ortho-sulphonic acid

The starting point in the preparation of the various compounds described in this paper was para-di-azo-toluene-ortho-sulphonic acid⁽¹⁾ of the formula



This was made in the following manner: 50 grams of finely powdered para-toluidine-ortho-sulphonic acid⁽²⁾ were made into a thin paste with 75 cc. of water in a 500 cc. flask. The flask was placed in a bath of ice-water, and a rapid current of the gas from nitric acid and arsenic trioxide passed into it, the flask being constantly agitated for from 1 to 5 minutes. The contents of the flask had a

(1). Rocher. Ann. Chem. 161, 8.

(2). Brackett and Hayes. Am. Chem. Jour. 9, 400

frothy appearance and granular
 crystals of the diazo compound had
 separated out. The current of gas was
 then stopped, and the diazo compound
 almost completely precipitated as a
 heavy granular mass, by the addition
 of about 30 cc of alcohol. After agita-
 ting for a few minutes, the contents
 of the flask were thrown on a filter,
 sucked with a pump, washed with
 alcohol then with ether, and dried.

In this manner, from 50 grams of para-
 toluidine-sulphonic acid, 42 grams of pure
 white diazo-toluene-sulphonic acid were
 obtained.

I. .3973 gr gave .0555 gr nitrogen

II. 3336 5468

Calculated for

Found

$C_7H_6O_3N_2S$

I

II

Nitrogen = 14.14 %

13.97 %

14.03 %

Para-fluor-toluene-sulphonic acid.

This acid was prepared by decomposing di-*ortho*-toluene-sulphonic acid with hydrofluoric acid in the following manner:

About 50 cc. of concentrated hydrofluoric acid were slightly warmed in a large platinum dish and 50 grams of the di-*ortho* compound dissolved in it. The di-*ortho* compound dissolved very readily. The solution was heated until decomposition, accompanied by evolution of nitrogen, began. The decomposition was allowed to take place slowly, and when complete, the contents of the dish were evaporated to a syrupy consistency, diluted with about two litres of water in a large porcelain

dark heated, neutralized with precipitated chalk, boiled with animal charcoal and filtered. The filtered solution gave a blue color with ferric chloride owing to the fact that some of the diazo-compound had been converted into para-mesol-sulphonic acid by the action of the water of the hydrofluoric acid solution. The calcium salt of the para-fluor-toluene-sulphonic acid was not obtained well crystalline, and sufficiently pure for analysis. The barium salt, however, (obtained by neutralizing with barium carbonate instead of precipitated chalk) was obtained in a very pure condition in small glistening scales. It was recrystallized until its solution no longer gave a color with ferric chloride and analyzed.

- 1.550 gr heated till constant weight lost .0235 gr.
 I { .5925 " dry salt gave .2704 gr. BaSO_4
 1.199 " heated till constant weight lost .0037 gr.
 II { 1.083 " dry salt gave .0477 gr. BaSO_4

	Calculated for	Found	
	$(\text{C}_7\text{H}_6\text{O}_3\text{SF})_2\text{Ba} + \text{H}_2\text{O}$	I	II
$\text{H}_2\text{O} =$	3.38 %	3.81 %	3.40 %
$\text{Ba} =$	26.60 "	26.83 "	26.63 "

As a qualitative test for fluorine, a small quantity of the salt was mixed with lime, & ignited in a platinum crucible, or fused with caustic potash in a silver crucible, dissolved in hydrochloric acid, (treated with a little calcium chloride if caustic potash has been used), & neutralized with ammonia. A precipitate of calcium fluoride was thus obtained, which when heated with sulphuric acid produced

an etching on a watch-glass. One of these tests was employed in all of the cases where fluorine compounds were made and fluorine was found to be present in all.

Potassium fluor-borane-sulphonate was made from the barium or calcium salt by heating with potassium carbonate. It crystallized from concentrated aqueous solution in large glass-like scales. It is very soluble in water. It may be precipitated as a granular powder by adding alcohol to the concentrated aqueous solution. The salt contains two molecules of water of crystallization.

$$\begin{aligned}
 & \left\{ \begin{array}{l} 50 \text{ grs. heated till constant weight } 0.8575 \text{ grs.} \\ 100 \text{ grs. dry salt gave } 2.7307 \text{ } 1.52 \\ 200 \text{ grs. dry salt gave } 5.5270 \text{ } \\ 75 \text{ grs. dry salt gave } 2.009 \text{ } 1.52 \end{array} \right.
 \end{aligned}$$

	Calculated for		Found
	$C_7H_6O_3SF_3K + 2H_2O$		
Br, O =	13.62 %	I	13.57 %
K =	17.14 "		17.19 "

A qualitative test showed the presence of fluorine

Para-chlor-toluene-ortho-sulphonic acid

This acid was made by decomposing diazo-toluene-sulphonic acid by hydrochloric acid in the same manner in which the chlor-toluene-sulphonic acid was made. Concentrated hydrochloric acid was used, and the product of decomposition was evaporated on the water bath until very little smell of hydrochloric acid remained.

The Barium Salt was made by adding the sulphuric acid with about twice the volume of water containing with barium carbonate. The mixture was

and charcoal filtering, and evapora-
 ting to dry residue. The residue was,
 as in the case of the decomposition
 with hydrochloric acid, gave a white
 color with ferric chloride due to the
 presence of the barium salt of bis-
 cresol-sulphonic acid. The barium
 salt of bis-cresol-sulphonic
 acid separated out in wart-like, a-
 morphous, granular aggregates. It
 was recrystallized until its solution no
 longer gave a color with ferric chloride.
 The salt is very little more soluble in
 hot than in cold water. It contains

no molecule of water of crystallization

$\left\{ \begin{array}{l} .2190 \text{ gr. heated till constant wt. lost } .0070 \text{ gr.} \\ .2120 \text{ .. dry salt gave } .0528 \text{ gr. BaSO}_4 \end{array} \right.$

$\left\{ \begin{array}{l} .37 - \text{ heated till constant weight lost } .015 \text{ gr.} \\ .3520 \text{ .. dry salt gave } .0905 \text{ gr. BaSO}_4 \end{array} \right.$

	Calculated for	Found	
		I	II
$(C_7H_5O_3SCl)_2Ba + H_2O$			
H ₂ O =	3.15%	3.20%	3.09%
Ba =	25.5%	25.5%	25.5%

This salt is identical with that prepared by Gussone and Scherer and Mayer.¹²

Potassium-chlor-rhene-sulphonate was made from the barium salt by treatment with potassium carbonate & crystallized from concentrated aqueous solution in light-yellow needles without water of crystallization.

I. .3191 gr gave .1139 gr K_2SO_4

II. .22200775 ..

	Calculated for	Found	
		I	II
$C_7H_5O_3SClK$			
Cl =	5.75%	5.50	16.11

¹² Ann. Chem. 72 230

¹³ Ber. 6 73

Para-mono-toluene-sulphonic acid

This acid was made by adding gradually 100 grams of diortho-toluene-sulphonic acid to 200 grams of hot concentrated hydrobromic acid, and continuing the heating until decomposition was complete.

The Barium Salt was prepared in exactly the same manner as that of the corresponding chlor-acid. It corresponds to the barium salt prepared by Jussieu, and Hübler and Post⁽²⁾. The solution gave the color reaction with ferric chloride showing that there also some thresol-sulphonic acid had been formed.

The Phosphonium Salt was made from the barium salt by treatment with

(1) - same element 72.25-

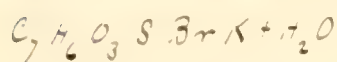
(2) - same element 69.15

potassium carbonate. This salt was
not described in literature and it
crystallized from concentrated aqueous
solution in thin lustrous scales.

2.105 gr heated till constant weight lost .0122 gr

986 .. dry salt gave .0598 gr K_2SO_4

Calculated for



Found

$H_2O = 5.86\%$

5.79%

$K = 13.50 ..$

13.50 ..

Para-nitro-toluene-ortho-sulphonic acid.

This acid was made by decomposing
diazo-toluene-sulphonic acid with hy-
driodic acid in the following manner:
50 grams of the diazo-compound were
placed in a flask with 250 c.c. of
absolute alcohol and 57 grams of con-
centrated hydriodic acid (57%) added

in near bottom the glass being
kept cool and agitated. When the
evolution of nitrogen had ceased, the
contents of the flask were gently
warmed in order to complete the de-
composition and the alcohol run
off. The residue was diluted with 5 or
6 litres of water, heated, neutralized
with lead oxide, and filtered while
boiling hot.

The Lead Salt was very difficultly
soluble and could not be complete-
ly separated from the excess of lead
oxide, by repeated boiling with water.
After boiling up or three times with
water, the residue was treated with a
solution of potassium carbonate, which
converted any undissolved lead salt
into the potassium salt which is
easily soluble. The hot solution of

the lead salt upon cooling, becomes covered with an iridescent scum of a grummy consistency. If, however the solution be evaporated to a small bulk this scum gradually thickens as the boiling is continued breaks up and falls to the bottom in heavy flakes which can easily be separated. The mother liquor upon further evaporation yielded another lead salt which was very soluble. These lead salts were not themselves further investigated, but were at once converted into potassium salts by treatment with potassium carbonate. The Potassium Salt obtained from the difficultly soluble lead salt by treatment with potassium carbonate, crystallized from moderate concentration aqueous solution in transparent,

whisker-shaped crystals, corresponding to the potassium salt of the 3-iodo-toluene-sulphonic acid described by Flusser. The salt contained iodine as was proved by a qualitative test, and crystallized with one molecule of water of crystallization.

.3200 gr. heated till constant weight lost .054 gr.
 I. { .3091 " dry salt gave .077 gr. K_2SO_4
 II. { .3090 " heated till constant weight lost .0150 gr.
 I. { .2931 " dry salt gave .0721 gr. K_2SO_4

	Calculated for	Found	
	$(C_7H_6O_3SIK) + H_2O$	I.	II.
$H_2O =$	5.08%	5.18%	5.14%
$K =$	11.61 "	11.11 "	11.03 "

The other potassium salt was much more soluble, and crystallized from concentrated aqueous solution in thin plates. The salt did not contain iodine. On analysis it

gave figures corresponding to the potassium salt of toluene-sulphonic acid

.08 gr. heated till constant weight lost .0132 gr.

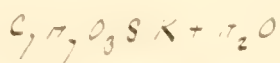
-.555 .. dry salt gave .0631 gr. K_2SO_4

.2865 .. heated till constant weight lost .0221 gr

-.20 .. dry salt gave .1090 gr. K_2SO_4

Calculated for

Found



I

II

$H_2O = 7.89\%$

7.82%

7.7%

K = 18.57%

18.19%

18.75%

The toluene-sulphonic acid from which this salt was formed, was undoubtedly formed by the further action of iodic acid upon the para-iodo-toluene-sulphonic acid, thus:



The acid with which the toluene-sulphonic acid is decomposed by the alkali

1) The time since 1875

own acids increases as we pass from sulphuric- to hydroiodic acid.

The dry potassium salts, fluor-, chlor-, brom-, and iodo-toluene-sulphonic acids thus obtained were treated in turn with phosphorus pentachloride and then with ammonia, thereby giving the sulphon-chlorides and amides. The details were as follows.

Para-fluor-toluene-ortho-sulphon-amide.

This was obtained by mixing together in a dish 50 grams of anhydrous potassium fluor-toluene-sulphonate, and 100 grams of phosphorus pentachloride; reaction taking place spontaneously, the mixture becoming hot & fuming. On stirring with an iron rod the greater part of the phosphorus pentachloride

and washing with cold water, the re-
sulting calcium chloride which was
obtained as a slightly yellow, viscous
liquid was allowed to drop slowly in-
to a dish containing about a liter of
strong aqueous ammonia. At first a bright
yellow color was shown. After being
stirred up with a bottle & shaken went
into solution. The solution was evaporated
to dryness on a water-bath, the residue
boiled with about 200 c.c. of alcohol and a
little animal charcoal, filtered and
evaporated to crystallization. The residue
crystallized from the moderately concentra-
ted alcoholic solution in large transparent
prisms, apparently orthorhombic, prisms
terminated by rhombic faces. It was easily
soluble in alcohol and hot water, solu-
ble with difficulty in cold water. From
an aqueous solution it crystallized in

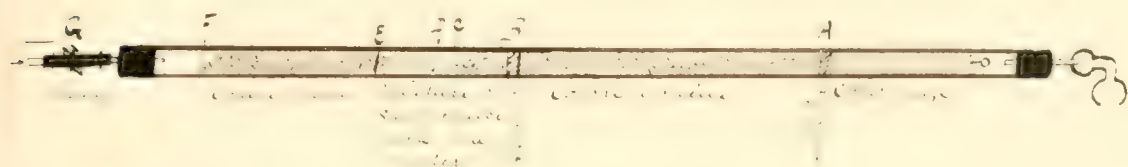
and the mixture. The melting point was 55° uncorrected.

The combustion analyses made of this anide, as well as of the various other compounds described hereafter were made as follows:

A mixture of about 4 parts by weight of finely divided lead chromate, and 1 part by weight of red lead, after being thoroughly washed was sucked into a compact mass on a funnel with a pump. While still moist the mixture was divided into lumps about the size of a pea, which were then heated to redness in a porcelain crucible, in small portions.

During the heating, stirring, or some of the lumps are broken up. When hot the mixture has a dark brown or black color which changes to a bright red on cooling in the air. The lumps after

particles are broken up in a mortar into
 grains about the size of sand which are
 separated by a sieve from the finer
 portions. The finer portions are powdered
 and used to mix with the substance
 to be analyzed. The tube is filled as
 follows:



A piece of reduced copper gauze is necessary
 whether the substance to be analyzed
 contains nitrogen or not. This is placed
 in front of an asbestos plug A. Behind
 this plug is placed the coarsely granular
 mixture to about two thirds the length
 of the tube. This is held in place by
 an asbestos plug E, and may be left
 unchanged so long as the tube is
 fit for use. Having the tube thus filled

from A to B, the remainder is filled as follows.

About two inches of the finely powdered preparation is introduced behind the plug B up to C. The weighed substance is then introduced, and about two inches more of the fine powder placed behind it. The substance is then intimately mixed with the fine powder by shaking & turning the tube. The remainder of the tube is then filled with the coarse grains up to F, and a passage made along the whole length of the tube by tapping it on a flat surface. The tube is placed in the furnace, connected in front with the calcium chloride tube *cc* and behind with an apparatus furnishing pure, dry air (or oxygen). The clamp at G is closed tight, & the tube heated red-hot from the front up nearly to B.

The tube is then heated from behind
forwards until it is all red-hot. When
the mixture containing the substance is
reached the gas jets are turned on gradu-
ally. When the bubbles of gas begin to
pass too slowly through the potash
bulbs, another jet is turned on &c.
When the tube has remained red-hot
throughout its entire length for some
time, and the gas has ceased to bubble
through the potash bulbs, the appa-
ratus is connected with an aspirator
which is set in operation and pure, dry
air drawn through to obtain the sample
at G, by which the rapidity of the current
of air can be regulated. The tube is
allowed to cool slowly while about
one litre of air is drawn through it.
The weighed tubes & bulbs are then dis-
connected, and the tube closed in front

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in connection with the various apparatus behind until cold.

The tube may be used a second time by removing everything up to the plug B from behind putting in a fresh piece of copper gauze if necessary and proceeding as before. The tube may be used so long as it is fit for use, without disturbing the portion between A and B. The advantage of the mixture of lead chromate and red-lead in this granulated form, is this, that it does not fuse down in the tube and presents a larger surface of action. It can be heated to a red-heat, and presents all of the advantages of copper oxide where copper oxide can not be used. The method has been used with good results in other granulations in the *Journal of the Chemical Society*.

In this method of analysis the following substances were used and the following results obtained:

- I. 3137 gr. gave .5003 gr. CO_2 and .1242 gr. H_2O
- II. 2535 098
- III. 153 137 (distillate)
- IV. 235 1682 .. $BaSO_4$ (barium)
- V. 255 1123 (..)
- VI. 238 316 (..)
- VII. 140 238 (..)

A qualitative test showed the presence of F.

Calculated for		Found						
	$C_{10}H_8O_2 \cdot SF_6$	I	II	III	IV	V	VI	VII
C =	44.44 %	44.28%	44.32%	—	—	—	—	—
H =	4.23 "	4.42"	4.38"	—	—	—	—	—
N =	7.41 "	—	—	7.33%	—	—	—	—
S =	16.93 "	—	—	—	16.44%	17.23%	17.03%	17.35%
F =	11.06 ..	—	—	—	—	—	—	—
O =	6.93 ..	—	—	—	—	—	—	—
	<u>00.00</u>							

(1) This analysis was made by Mr. H. B. Skolfield of the U.S.

Para-chlor-Toluene-sulphon-amide

This was ^{made} in exactly the same manner as the Fluor-toluene-sulphon-amide. It was easily soluble in alcohol and hot water, soluble with difficulty in cold water. It did not crystallize well from alcohol. From hot aqueous solution, it crystallized on cooling, in long white needles.

The melting point was 45° (uncorrected). This amide corresponded to that of Heller⁽¹⁾. On analysis the following figures were obtained:

I.	.2819 gr.	gave	.4210 gr. CO_2	and	.1021 gr. H_2O
II.	.302145181077 ..
III.	.51610356 ..	nitrogen (Kjeldahl)	
IV.	.49010337	(..)
I.	.44254532 ..	BaSO_4	(Barium)

- I .2718 gr. gave .3045 gr. Ba SO₄ (Pearson)
- VII .34562392 .. Ag Cl (Burning with lime)
- VIII .43873031 (.. ..)

Calculated for		Found							
C ₈ H ₆ O ₂ NSCl		I	II	III	IV	V	VI	VII	VIII
C =	40.88 ⁹ / ₁₀	40.73%	40.79%	—%	—%	—%	—%	—%	—%
H =	3.89..	4.02"	3.96"	—"	—"	—"	—"	—"	—"
O =	15.57..	—"	—"	—"	—"	—"	—"	—"	—"
N =	6.51..	—"	—"	6.89"	6.85"	—"	—"	—"	—"
S =	5.57..	—"	—"	—"	—"	5.45	5.37	—"	—"
Cl =	7.28..	—"	—"	—"	—"	—"	—"	—"	—"
100.00..									

Para-nitro-fluore-sulphonamide.

This was made from potassium-fluore-sulphonate in the same manner as the corresponding fluor- and chlor-amides. The amide agreed with that prepared by Jussen⁽¹⁾ & Hübin & Post⁽²⁾

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(2) 1169, 15

Pentachloro-toluene-sulphonic-amide.

This was made by rubbing together in a dish, 50 grams of anhydrous potassium iodo-toluene-sulphate, and 100 grams of phosphorus pentachloride. Action took place spontaneously, the mixture becoming hot & liquid. The resulting sulphur-chloride, after driving off most of the phosphorus oxychloride and washing with cold water was obtained as a white, soft-solid. When this was added to about a litre of strong aqueous ammonia it did not all go into solution on boiling as did the corresponding nitrogen compounds, but it was all converted into the amide nevertheless. This amide is, therefore, not so solu-

ble in ammonia as the corresponding
amides of the fluor- chlor- & brom-
sulfonic acids.

The contents of the dish were evapora-
ted to dryness on the water bath,
boiled with about 200 cc. of alcohol &
a little animal charcoal, filtered,
and evaporated to crystallization.
From the concentrated alcoholic solution,
the amide crystallized in fine white
needles. It is ~~very~~ soluble in alcohol,
only sparingly soluble in hot water,
from which on cooling it crystallizes
in white needles finer than those from
alcoholic solution. The melting point was
 185° to 187° (uncorrected). The amide agreed
with the amide of β -iodo-toluene-
sulfonic acid prepared by Glasner.¹⁾
On analysis the following numbers
were obtained.

(1) Ber. 8, 561

I.	.9.0 gr.	gave .2011 gr CO_2 and .0566 gr H_2O
II.	.220022430658
II	.5022360 .. nitrogen (yielding) (1)
II.	.2080671 .. AgI. and .640 gr. BaSO_4 (Carus)
I.	.253920062003 (..)

Calculated for

Found

	$\text{C}_7\text{H}_5\text{S}_2\text{N}_2\text{I}$	=	=	=	I	V
C:	28.28%	28.71%	27.80%	—%	—%	—%
H:	2.69 ..	3.29 ..	3.32 ..	— ..	— ..	— ..
O:	1.78 ..	— ..	— ..	— ..	— ..	— ..
N:	7.71 ..	— ..	— ..	4.64 ..	— ..	— ..
S:	1.78 ..	— ..	— ..	— ..	0.82 ..	0.83 ..
I:	— ..	— ..	— ..	— ..	2.54 ..	2.71 ..
	100.00					

These substances under other analysis by means of an alkaline solution of potassium permanganate, yielded respectively fluor-chlor-brom- and iodo-sulphide. The ber-

(1) This analysis was made by Mr. C. E. Sanderson

centage of sulphuric acid obtained was, in all cases, considerably less than the theoretical yield, although the oxidation was conducted under a variety of conditions. The best conditions which were known for obtaining the largest yield of the amide were in the case of one of them as follows.

First, the amide must be free from foreign substances, as a small amount of the impurities which are liable to occur in the preparation of the amide, greatly affects the result.

20 grams of the amide and 8 grams of caustic potash are dissolved in 2 litres of water, in a 3 litre flask. The flask is placed in a bath of boiling water, and a concentrated solu-

tion of 35 grams of potassium permanganate added a little at a time. The flask is kept in the bath of boiling water until all of the permanganate is used up, or only a slight pink color remains. This requires as a rule from 5 to 8 hours. A little alcohol is then added, and the contents of the flask filtered, the residue washed with hot water, & the filtrate evaporated to about 75 cc. While still warm the sulphuric anhydride with some monoxigen anhydride is precipitated by the addition of strong hydrochloric acid. When cold, the contents of the dish are thrown on a filter sucked with a pump, & washed with a little cold water. In order to separate the monoxigen anhydride from the sulphuric, the mixture is boiled with water, neutralized

with precipitated chalk, filtered
and allowed to cool, when the
amide crystallizes out of the solution
in long white needles, and is sepa-
rated. The solution on further evapo-
ration yields the calcium salt of
the sulphide. The calcium salts
of para-fluor-, para-chlor-, para-brom-,
and para-iodo-sulphide all crys-
tallize from concentrated aqueous so-
lution in radial groups of white needles.
These salts have the same tastes as
the sulphides themselves. In analysis
the following figures were obtained.

Calcium salt of para-fluor-sulphide

I { .1876 gr heated till constant weight lost .0439 gr.
.1437 .. dry salt gave .0446 gr CaSO_4

.2037 gr. heated till constant weight lost .0500 gr.
 II { .1561 .. dry salt gave .0488 gr CaSO_4

Calculated for		Found	
$(\text{C}_7\text{H}_3\text{O}_3\text{NSF})_2\text{Ca} \cdot 7\frac{1}{2}\text{H}_2\text{O}$		I	II
$\text{H}_2\text{O} =$	23.48 %	23.40 %	23.37 %
$\text{Ca} =$	9.09 ..	9.13 ..	9.19 ..

Calcium salt of bar. chlor. sulphuride

.2514 gr. heated till constant weight lost .0560 gr.
 I { .1954 .. dry salt gave .0553 gr. CaSO_4

.255 .. heated till constant weight lost .0560 gr.
 II { .1954 .. dry salt gave .0565 gr CaSO_3

Calculated for		Found	
$(\text{C}_7\text{H}_3\text{O}_3\text{NSCl})_2\text{Ca} \cdot 7\frac{1}{2}\text{H}_2\text{O}$		I	II
$\text{H}_2\text{O} =$	22.20 %	22.27 %	22.31 %
$\text{Ca} =$	8.70 ..	8.32 ..	8.50 ..

Calcium salt of para-iron-sulphinic

This salt was prepared by Remsen and Bayley. It gave figures corresponding to the formula $(C_7H_3O_3NSI)_2Ca + 7\frac{1}{2}H_2O$

Calcium salt of para-iron-sulphinic

I { .2575 gr. heated till constant weight lost .0439 gr.
 .2136 .. dry salt gave .0440 gr $CaSO_4$

II { .2482 .. heated till constant weight lost .0422 gr.
 .2060 .. dry salt gave .0421 gr $CaSO_4$

	Calculated for	Found	
	$(C_7H_3O_3NSI)_2Ca + 7\frac{1}{2}H_2O$	I	II
H_2O =	17.07%	17.05%	17.00%
Ca =	6.10 ..	6.06 ..	6.0 ..

The sulphinides themselves were obtained as precipitates, by adding hydrochloric acid to

The saturated solutions of these represent calcium salts. They are all difficultly soluble in cold water, & still more so in hydrochloric acid.

Para-Thior-Sulphuric

This was made from its calcium salt by precipitation with hydrochloric acid. It is moderately soluble in hot water, from which on cooling it crystallizes in long white needles which break up on drying into granules. When crystallized slowly from dilute solution it crystallizes in small transparent rhombs. Its taste was at first purely sweet, but after remaining in the mouth for a few minutes, a slight bitter after-taste was perceptible. Its sweetness as could be judged, was somewhat less than that of benzoic sulphuric.

more. The melting point was 203-204° (subl.)
 It gave on analysis the following figures:

- I. .5086 gr. gave .772 gr. CO_2 and .097 gr. H_2O
- II. .398060800746
- III. .787333370 .. nitrogen (Dumas)
- IV. .50080347 (..)
- I. .37093953 .. $BaSO_4$ (Pearson)
- II. .18562096 (..)

— analysis and found the amount of fluorine.
 Calculated — Found

	C. H. N. S. F.	I	II	III	IV	V	VI
C =	55.5	55.5	55.5	55.5	55.5	55.5	55.5
H =	2.2	2.2	2.2	2.2	2.2	2.2	2.2
N =	23.8	23.8	23.8	23.8	23.8	23.8	23.8
S =	6.5	6.5	6.5	6.5	6.5	6.5	6.5
F =	10.5	10.5	10.5	10.5	10.5	10.5	10.5
	<hr/>						
	100.00						

Para-chlor-sulphinide.

This was made from its calcium salt by precipitation with hydrochloric acid. It was not quite so soluble as para-thion-sulphinide. It crystallized from hot aqueous solution, on cooling, in thin plates. The melting point was 218° (uncorrected). It had both a sweet and a bitter taste. Both tastes were very marked, but the bitter seemed to be the more intense of the two. This substance was prepared in small quantities by Mr. Kettle of the Johns Hopkins University, in order to ascertain its effect upon the nerves of taste. It was not further studied in this. I have obtained on analysis the following figures.

Para-brom-sulphamide

This was made from its calcium salt by precipitation with hydrochloric acid. It was slightly less soluble than para-chlor-sulphamide. It agreed in all respects with that prepared by Remsen and Bayley¹⁾. It possessed both a sweet and a bitter taste, but in a less marked degree than para-chlor-sulphamide. The yield obtained by conducting the oxidation of the sulphamide under the conditions mentioned conditions, was larger than was obtained by Remsen and Bayley. The yield was 0 to 12 percent of the theoretical.

Para-iodo-sulphamide

This was obtained from its calcium salt

¹⁾ Am. Chem. Jour. 9, 225

by precipitation with hydrochloric acid. It was the least soluble of the halogen sulphurides. It crystallized from hot aqueous solution, in which it gave white needles. Its melting point was $230^{\circ}\text{--}232^{\circ}$ (uncorrected). Its taste was not very marked, being only slightly bitter with no sweet taste whatever. On analysis the following figures were obtained:

I.	.3220 gr.	gave .3441 gr. CO_2 and .0414 gr. H_2O	
II.	.2621 ..	.2632 ..	.0324 ..
III.	.2577 ..	.2883 ..	.0361 ..
IV.	.32 ..	.3273 ..	nitrogen (Kjeldahl)
V.	.30 ..	.0309 ..	(Nieldahl)
VI.	.8 ..	.370 ..	AgI and .387 gr BaSO_4 (Carus)
VII.	.2327 ..	.1776 ..	.1769 .. (..)

Calculated =

Found

	..	I	II	III	IV	V	VI	VII
C =	27.15%	27.28%	27.35%	27.33%	—	—	—	—
H =	2.5 ..	1.64 ..	1.37 ..	1.6 ..	—	—	—	—

C = 55.5
 N = 5.5
 S = 1.48
 H = 1.48

It is well known that by boiling with
 dilute manganic acid benzoic
 sulphide is converted into the
 acid ammonium salt of ortho-sub-
 stituted benzoic acid. It was thought very
 probable that by similar treatment
 the para-halogen-sulphides would
 behave in the same manner. This
 was found to be the case with para-
 chlor-sulphide. The other halogen-
 sulphides were not investigated
 in regard to this point. They would
 probably act in the same way.
 5 grams of para-chlor-sulphide were

boiled with dilute hydrochloric acid for about an hour the flask being connected with a reflux condenser. The contents of the flask were then concentrated to dryness, & heated on the water-bath until all smell of hydrochloric acid had disappeared. The residue was dissolved in water, in which it was easily soluble. The solution had no taste and on slow evaporation gave crystals similar in appearance to the acid ammonium salt of ortho-sulpho-benzoic acid. It was shown by analysis to be the acid ammonium salt of para-chlor-ortho-sulpho-benzoic acid.

2.5372 gr. gave .0359 gr. NH_3

2.890 " " .032 " "

Calculated for $C_6H_4(COOH)(SO_2NH_2)Cl$

$NH_3 = 6.71\%$

Found
 $= 6.65\%$
 $= 6.50\%$

Conclusions

The relative degrees of sweetness and bitterness can not be very roughly measured. It is also impossible to make accurate comparison between a sweet and a bitter taste as regards the relative intensity of the two. There is also a difference of opinion amongst those who have tasted these substances. The majority, however, were of the opinion that the substances have the tastes described in the preceding pages. These may be tabulated thus:

Para-chlor-sulphuric acid	= SWEET.	> Bitter
Chloroform	= Sweet	< Bitter
Carbon tetrachloride	= Sweet	< Bitter
Chloroform	= —	Bitter

Biographical Sketch

The author of this paper, Rudolph John Julius de Rode was born on August 2nd 1857 in Lexington, Fayette County, Kentucky. He graduated as Bachelor of Science at the State College of Kentucky in June 1885 and obtained the degree of Master of Science at the same institution two years later. He was employed as Assistant Chemist at the Kentucky Agricultural Experiment Station from September 1885 till September 1886, at which time he entered the Johns Hopkins University as a candidate for the degree of Doctor of Philosophy, with Chemistry, Mineralogy and Geology as his subject of study. He was appointed Lecturer

Assistant to Prof. Ruess 1885,
and Fellow in Chemistry in 1886.

John F. Johnson, President, March 1887.

